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9**International Journal of Heat and Mass Transfer 90 (2015)** 752–760 **Contents lists available at ScienceDirect International Journal of Heat and Mass Transfer journal homepage: www.elsevier.com/locate/ijhmt A**

11**study on the method of short-time approximation – Criteria for applicability Alvin Casandra** a, **Suryadi Ismadji** b, **Boris A. Noskov** c, **Libero Liggieri** d, **Shi-Yow Lin**

a,⇑ a

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Surfactant Short-time approximation Diffusivity Dynamic surface tension Ward–Tordai equation Planar surface abstract Despite

4**its widespread use in the determination of adsorption mechanisms and the estimation of** surfac- tant **diffusivity,**

the short-time approximation method, used for linearly fitting experimental dynamic surface tension data, should be validly applied

2**only over a very specific range of time** intervals **or surface** pressures. **Therefore,** the definition of **general criteria for the applicability of this**

method and for error evaluation in diffusivity estimations is fundamental.

2**In this work, a theoretical** numerical **simulation of the short-time approximation** method **was conducted,** and general benchmarks **for**

its accurate utilization were investigated. Specifically, for systems assuming planar gas–liquid surfaces, diffusion-controlled kinetics and a Langmuir adsorption isotherm, simple rules were developed

2**in terms of limiting surface pressure** (pmax) **and dimensionless time (t/max) as a function of dimensionless surfactant concentration (C0/a).**

For values greater than the limiting (maximal) conditions, the dynamic surface tension curve deviates from the short-time approximation straight line, and thus, the corresponding linear fitting could lead to significant errors in evaluating the diffusivity. The simple criteria proposed in this study thus precisely define the range of applicability for the short-time approximation method. Ó 2015 Elsevier Ltd. All rights reserved. 1. Introduction Surfactants are essential agents in

3**sundry practical applications and products,** including **detergents, inks, adhesives,** pesticides, **and cosmetics**

[1]. In recent years, the global market for surfactants has shown rapid growth, with a 3.8% annual increase: in 2012, the market value was estimated at approximately US$26.8 billion, and it is expected to reach US$31.1 billion by 2016 [2]. Because surfactant optimization depends on specific knowledge of their dynamic adsorption behavior [3], it is not surprising that this field of study

3**has gained tremendous attention over the past two decades.**

In 1946, Ward and Tordai introduced a general equation for interpreting the surfactant adsorption kinetics of planar gas–liquid surfaces [4]. In their model, the authors assumed that surfactant diffusion from the bulk to the sublayer is the limiting step com- pared to surfactant

10**transfer from the sublayer to the** surface. This **diffusion-**

controlled approach has been observed to be valid for ⇑

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the majority of small, pure surfactants and surfactant mixture sys- tems [5] such that the equation describing their behavior is consid- ered a fundamental starting point in numerous models used today. However, the Ward–Tordai equation is rather complex, and its application has been hindered for decades by its complicated numerical calculations. Therefore,

3in 1959, Defay and Hommelen [6] and Hansen and Wallace [7] introduced a simplified form of the equation, assuming that surfactant backward diffusion

from the sublayer to the bulk solution could be omitted for initial short time intervals.

3In 1979, van den Bogaent and Joos [8] coupled this simplified equation with the Gibb's adsorption equation and

von Szyszkowski's equation, developing an easy-to-use linear approxi- mation for the Ward–Tordai equation. Due to its simplicity, this short-time linear approximation equation has been widely used to date [9–41]. Specifically, many researchers [10,14–17,19,20,22,23,25,27–32,34,35,37,38,40] have utilized the equation to evaluate surfactant diffusivities or deter- mine the adsorption mechanism of various systems, linearly fitting dynamic surface tension data with the short-time linear approxi- mation equation (c vs. t1/2) for specific ranges of ''short'' time inter- vals (generally t1/2 = 0–5s1/2, but up to t1/2 = 200s1/2 in [22]). A detailed literature review of these diffusivities, estimated by using the short-time approximation method, is reported in Table 1. Intuitively, because dynamic surface tension data can be accu- rately linearly fitted only for specific initial time intervals, an appropriate choice of the time range plays a crucial role in the cor- rect evaluation of diffusivity. In fact, it has been reported [22,23,25,28] that quite diverse values of diffusivity have been observed when different time ranges were chosen. Ultimately, thus, certain general criteria for validly applying the short-time approximation method would be essential to guiding researchers in correctly estimating diffusivities. Therefore,

2in this work, a theoretical numerical simulation of the short-time approximation method was conducted, and general benchmarks for

its accurate utilization were investigated. All cal- culations were carried out for a

16**diffusion-controlled adsorption** process involving **the** mass **transport of surfactant molecules from** a uniform **bulk** phase **to**

a freshly created air–water interface. The following conditions were applied: (1) a Langmuir adsorption isotherm, (2) a planar air–water interface, (3) room temperature 25 °C, and (4) a diffusivity of Dset = 5 10 6 cm2/s for different dimensionless surfactant concentrations (the

4**ratio between the bulk concentration and the surfactant activity)**

C0/a. Additional simulations were conducted for different a values. 2. Theoretical framework 2.1. Ward–Tordai equation In the case of one-dimensional

7**diffusion and adsorption onto a planar surface from a bulk phase**

initially containing a uniform dis- tribution of a surface active solute, the diffusion of the surfactant in the bulk continuous phase is described by Fick's law: @C @2C @t ¼ D @z2 ðz > 0; t > 0Þ ð1Þ where z is the distance from the surface and C(z, t) is the bulk con- centration of surfactant molecules. The boundary and initial condi- tions for Eq. (1) are as follows: Cðz; tÞ ¼ C0ðz > 0; t ¼ 0Þ ð2Þ Cðz; tÞ ¼ C0ðz ! 1; t > 0Þ ð3Þ CðtÞ ¼ 0ðt ¼ 0Þ ð5Þ dC @C dt ¼ D @z ðz ¼ 0; t > 0Þ ð4Þ Table 1 A literature review of experimental estimates of the diffusivity (D) for different systems, predicted by using the short-time approximation method for different time intervals (t). Refs Compound D (10 6 cm2/s) C0 (mol/cm3) t1/2 (s1/2) p a (mN/m) Model parameter e C1

6**(10 10 mol/cm2) a (10 10 mol/cm3)**

13 Glu8-2-Glu8 Glu12-2-Glu12 16 FluoroCarbon4 17 C9-TGE b 19 C12-Maltose ester 20 ANHG550 c 22 Pluronic F68 23 C10E6 25 di-C8 27 C8DMPO d C10DMPO d 28 C10E4 29 b-lactoglobulin b-casein 30 DPPC 31 Hexanol 32 MTAB 33 Triton X-405 34 TDSNa 35 SDS 37 Na-myristate + Na-Decanoate 38, 40 DC10PO DC12AO 1.5 3.5 10 6 0.17 2.3 1 10 8 2 10 8 1.1 2.6 10 8 3.4 0.8 10 6 2.4 0.32 10 6 2.6 1.2 10 6 0.92 0.17 10 11 0.92 0.72 10 11 57 8 10 8 3.0 2 10 7 5.3 4 10 7 20 10 7 4.8 2 10 7 20 10 7 4.9 0.05 10 6 0.6 10 6 4.9 0.1 10 9 5 10 9 4.9 0.1 10 9 5 10 9 12 2 10 9 8 10 10 9 1.5 5 10 6 0.39 10 10 6 13.4 4 10 8 0.7 2.54 10 8 7.63 10 8 2.0 2 10 6 4.7 0.5 10 6 2.8 2 10 6 1.1 2.25 10 7 + 1 10 5 0.029 0.29 10 7 0.011 1.1 10 7 0.4 4.37 10 8 17 10 8 0.1–0.3 6.0 0.1–0.2 0.6 0–14 6.0 0–14 13 0–3 3.5 0–0.3 3.0 0–0.65 2.0 0–0.2 10 0–200 3.0 0–30 4.0 0–0.4 22 0–0.55 7.0 0–0.09 2.0 0–0.05 7.5 0–0.2 1.5 0–0.05 17 0–1.6 2.0 0–0.9 17 0–30 0.5 0–12 17 0–30 1.0 0–30 14 0–19 5.8 0–17 15 0–0.07 9.0 0–0.03 12 0–1 5.9 0–0.21 0.1 0–0.20 1.0 0–0.09 14 0–3 4.0 0–3.1 12 0–1 7.3 0–8 4.4 0–6 11 0–10 7.2 0–8 15 3.99 4.23 4.39 0.31 10.0 63.8 2.46 8.06 3.34 55.8 2.13 4.40 4.84 0.021 2.30 10.8 2.81 1.68 3.20 3830e 3.60 420e 3.18 25.7 1.88 2.02 4.87 0.77 2.79 2.71e 6.86 52100 2.80 3600e 0.92 0.22 9.24 4030e 3.84 16000e 3.08 38800e 3.70 330e 4.20 280e a Surface pressure, p = c0 c. b TGE = tryptophan glycerol ether surfactant. c ANHG550 = heterogeminis surfactant of PEG with MW = 550. d DMPO = dimethyl phosphine oxides. e Parameters (C1 and a; maximum surface concentration and surfactant activity) obtained from previous studies. where C0 is the initial bulk

concentration, C is the surface concen- tration of surfactant and zero C indicates an initially clean air–wa- ter surface. By using the Laplace transform, the adsorption of surfactant molecules

12**as a function of time can be** formulated **in terms of**

an unknown sublayer concentration CS(t) = C(z = 0, t): CðtÞ ¼ 2C0 Dt 1=2 2 D p p p 1=2 Z pffit CSðt sÞd sffiffiffi ð6Þ 0 where CS

5**is the** sublayer **concentration and D is the surfactant** diffu- sivity. **This** relation **is the**

well-known Ward–Tordai equation, which is applicable for an initially clean planar gas–liquid surface and a diffusion-controlled surfactant mass transport process. This sublayer concentration can be determined numerically [42] by a modification of the technique used by Miller and Kretzschmar [43]. Specifically, the first and second terms on the right-hand side of Eq. (6), defined in this work as TermF and TermB, are linked to sur- factant forward

10**diffusion from the bulk phase to the sublayer and** surfactant backward diffusion **from the** sub-layer **to the**

bulk solu- tion, respectively. 2.2. Dynamic surface tension To obtain the theoretical dynamic surface tension curve, the Ward–Tordai equation (6) has to be combined with two additional relations: the

13**adsorption isotherm and the equation of state. The** adsorption isotherm relates **the surface**

concentration and subsurface concentration of surfactant molecules at constant tem- perature. When

15**it is assumed that the mass transport** process **is** diffusion **-controlled** and **the**

adsorbed surfactants on the surface do not interact with each other, the Langmuir isotherm can describe the

13**relationship between the surface** concentration **and** the **bulk surfactant concentration:** C1 ¼ x ¼ **C**

C aþC ð7Þ where C1 and a are the model parameters of the Langmuir iso- therm, and x is the dimensionless surface concentration. Parameter C1

3is the maximum surface concentration and a indi- cates the surfactant activity. The

3Ward–Tordai equation (6) coupled with the Langmuir adsorption

isotherm (Eq. (7)) can be solved numerically to obtain C(t). Finally, the

5equation of state determines the dependence of the surface tension on the surface concentration:

cðtÞ ¼ c0 þ RTC1ln½CðtÞ=C1Š ð8Þ

19where R is the universal gas constant, T is temperature and c0 is the surface tension of solvent.

2.3. Short-time linear approximation method At the

10beginning of the adsorption process (t 0),

surfactant backward diffusion from the sublayer to the bulk phase can be assumed to be negligible, such that TermB of the Ward–Tordai equation (6) can be omitted, and the surfactant surface concentra- tion C at a time t is given by CðtÞ ¼ 2C0 rffiDffiffiffiffitffi p ð9Þ The Gibbs adsorption equation relates the surface tension (c) to the surface concentration (C): dc ¼ RTCdlnC ð10Þ Integrating Eq. (10) and applying Eq. (9) yields the following: Z c dc ¼ Z CS RTC dCS ¼ 2C0RT rffiDffiffi Z CS tffiffi p dCS ð11Þ 0 0 CS p 0 CS If the term ffitffiCS is considered to be constant during the initial p stage of the adsorption process with initial condition (5) [C(t = 0) = 0, i.e., CS(t = 0) = 0], the following relation is obtained: cðtÞ c0 ¼ 2C0RTrDffipffiffi pCStffiffi Z CS rDffiffiffiffiffiffitffiffi dCS ¼ 2C0RT ð12Þ 0 p which leads to the so-called short-time approximation equation and a linear relationship between c(t) and t1/2. It should be noted that Eq. (12) holds for a diffusion-controlled adsorption process. As illustrated in the introduction, for decades, Eq. (12) has been used by many researchers [10,14–17,19,20,22,23,25,27–32,34,35, 37,38,40] as an easy method for determining a diffusion- controlled adsorption process and for estimating surfactant diffu- sivity. A linear dependence between c(t) and t1/2 is commonly used to determine whether an

17adsorption process is diffusion-controlled [8], and the surfactant diffusivity is estimated by

simply linearly fitting the initial slope of the c(t) curve in the c(t) t1/2 plot by set- ting this slope equal to 2RTC0 pffiDffiffiffi=ffiffipffiffiffi: 3. Results To determine the valid ranges of applicability of the short-time

approximation technique for identifying adsorption mechanisms and estimating diffusivity, a theoretical numerical simulation was performed in this study. All calculations were carried out for an established diffusivity of Dset = 5 10 6 cm2/s and for different dimensionless bulk concentrations C0/a. Initially, by using the Ward–Tordai equation and the Langmuir adsorption isotherm, with parameters C1 = 5

6**10 10 mol/cm2** and **a** = 1 **10** 9 **mol/cm3**

as delineated in Section 2, the exact relaxation curves of the dynamic surface tension, c(t), and the sur- face concentration, C, were generated for five different values of C0/a, as shown in Fig. 1a. Plotting the surface tension (or surface pressure) as a function of t1/2, initially linear trends (as predicted by Eq. (12)) were clearly identified for specific short time intervals (Fig. 1b). A decrease in the time intervals (denoted tmax in this study) is noted, in which the theoretical curves show linear behav- ior with increasing bulk concentration for a = 1 10 9 mol/cm3. The data in Fig. 1b indicate that t1m/2ax decreases from 80 s1/2 to 32 s1/2 as C0/a increases from 0.4 to 8. In other words, tmax decreases from 6400 s to 1024 s as C0/a increases from 0.4 to 8. A surface pressure (denoted pmax) corresponding to tmax is therefore defined, in which the theoretical curves show a linear c vs. t1/2 behavior. Fig. 2 shows the change in tmax

5**as a function of** surfactant **concentration for surfactants** with **different**

surfactant activities, a = 1, 5, and 20 (10 9 mol/cm3). For surfactants with different activities, tmax always decreases with bulk concentration. Moreover, a dramatic decrease occurs at a C0/a value of approxi- mately 8. Fig. 3 details the deviation in c(t) between the tension data (cdata) predicted by the Ward–Tordai equation and those (capprox) determined by the short-time approximation (Eq. (12)) at t < tmax; Dc(t) = cdata–capprox. The data in Fig. 3 indicates for the case of C0/a = 8, a positive deviation occurs at the beginning, followed by a negative Dc(t); then, another positive value of Dc(t) occurs. The maximum deviation in c in this case is 0.7 mN/m, which is roughly the measurement uncertainty in our experiments. Fig. 4 summarizes the relaxation of Dc(t) for different surfactant concen- trations, C0/a = 0.4–30. At intermediate surfactant concentrations (2.2–8), the deviation in Dc(t) is similar to the behavior shown in Fig. 3. When the concentration is low (C0/a = 0.4–2), Dc(t) shows a small negative value, followed by a small positive one. In a b Fig. 1. Relaxation profiles generated using the Ward–Tordai equation and the Langmuir isotherm (C1 = 5

6**10 10 mol/cm2, a** = 1 **10** 9 **mol/cm3,**

and Dset = 5 10 6 cm2/s). Profiles of (a) c(t), C(t) and (b) p(t1/2) for five different values of C0/a (=0.4, 1, 2, 4, 8). 104 A 103 t max (s) 102 B 10 C 1 10-1 0.1 1 C0 /a 10 Fig. 2. Relaxation of tmax

2**as a function of surfactant concentration C0/a**

and surfactant activity: a = 1 (A), 5 (B), and 20 (C) (10 9 mol/cm3). 70 γ (mN/m) 60 50 0.8 0.4 0 Δγ (mN/m) t1/2max= 32 -0.4 C0 /a = 8 -0.8 0 10 20 30 40 t1/2 (s1/2) Fig. 3. Deviation in surface tension Dc (t) between the c(t) data (solid curve, cdata) and the linear prediction (dashed line, capprox) of the short-time

approximation for C0/a = 8; Dc(t) = cdata–capprox. 0.8 C0/a=8 6 0.4 4 3.5 2.5 3 Δγ (mN/m) 2 0.4 0 1 4 0.1 6 C0/a=3.5 3 2.2 2.2 1 -0.4 8 Δγ 2.5 0 2 2.5 2 3 3.5 0.4 30 12 10 -0.8 0 10 20 t1/2 30 40 50 0 20 40 t1/2 (s1/2) 60 80 Fig. 4. Relaxation of the tension deviation Dc (t) at different surfactant concentrations C0/a. contrast, at high concentrations (C0/a > 10), a significantly positive value of Dc(t) occurs first, followed by a negative one . In applying the short-time approximation technique, experi- mental dynamic surface tension data are linearly fitted (lines 1 in Fig. 5) to estimate the surfactant diffusivity when an adsorption process is diffusion-controlled. Fig. 5 illustrates the fitting and the evaluation of the diffusivity D using the short-time approximation technique for the early stages of the dynamic c(t) data derived from the Ward–Tordai equation. For surfactant concentrations (C0/a) lower than 2 this linear fitting calculation leads to an underestimation of the diffusivity (Fig. 5a), whereas for C0/a values greater than 2, D is overestimated (Fig. 5c). In both cases, the devi- ation from the established value Dset increases with the time range considered such that, intuitively, shorter time intervals lead to more precise estimates of the diffusivity (lines 2 in Figs. 5a and c). Interestingly, as previously noted, for C0/a = 2, the deviations in the estimated D (shown as the line 1 in Fig. 5b) from Dset (shown as the line ‘‘2’’ in Fig. 5b) are negligible for all time ranges, where the c(t) t1/2 curve follows a linear trend. This deviation in the estimated value of D (underestimation at low C0/a, nearly zero deviation at C0/a = 2, and overestimation at large C0/a) is derived from the deviation in the tension Dc(t) shown in Fig. 4. At low concentration, Dc(t) < 0 first, then Dc(t) > 0 over time (Figs. 4 and 5a). The positive Dc(t) deviation causes a smaller D value to be estimated by linear fitting (Eq. (12)); therefore, D is underestimated. At high concentration, Dc(t) > 0 first, then Dc(t) < 0 over time (Figs. 4 and 5c). The nega- tive Dc(t) deviation causes a larger D value to be estimated by lin- ear fitting; therefore a D is overestimated. At C0/a = 2, Dc(t) is small; therefore, the effects induced by positive and negative val- ues of Dc(t) are balanced, resulting in a small deviation in D. The data in Figs. 5a and c lead to another conclusion: a larger deviation in D is observed when a larger range of c(t) data is used for the short-time approximation. Fig. 5c shows that D = 7.7 10 6 cm2/s was obtained when the c(t) data at t1/2 < 20 s1/2 were used. When the c(t) data at t1/2 < 32 s1/2 were used, a larger deviation in D (8.6 10 6 cm2/s) was observed. The effect of surfactant concentration (C0/a) on the deviation in D (Derr = 100(Dapprox–Dset)/Dset) is shown in Fig. 6. A nearly linear dependence was observed when Derr was plotted

17**as a function of surface pressure** p. **The** value **of**

p indicates the range of c(t) data used for linear fitting by the short-time approximation technique. This linear dependence confirms the conclusion discussed above: a larger deviation in D is observed when a larger range of c(t) data is used. Fig. 6a also indicates that at high concentrations, a larger range of c(t) data can be used for evaluating D in applying the short-time approximation technique. The last data point (solid cir- cle) indicates the maximum range of c(t) data over which the ten- sion deviation [Dc (t) = cdata –capprox] is still allowable (less than the measurement uncertainty; 0.1 mN/m at low surfactant 72 a γ (mN/m) D = 4.07 (10-6 cm2/s) 71 2 3.38 3 2 1 70 1 0 20 40 60 t1/2 (s1/2) 100 72 b 70 γ (mN/m) 68 D = 4.94 (10-6 cm2/s) 66 64 1 2 1 0 10 20 30 40 t1/2 (s1/2) 60 70 c D = 7.68 (10-6 cm2/s) γ (mN/m) 60 8.63 2 2 3 50 1 1 0 10 20 t1/2 (s1/2) 30 40 50 Fig. 5. The linear behavior, c(t)-t1/2, determined by the short-time approximation at different surfactant concentrations for the data shown in Fig. 1 (line 1): C0/a = 0.4 (a), 2.0 (b), and 8.0 (c). Lines 1 and 2 shows the effect of the time interval used on estimating the diffusivity (lines 2 use a short interval than lines 1). Line 3 shows c(t) derived from the short-time approximation with Dset = 5 10 6 cm2/s. 80 a C0/a = 8 21.0 40 Derr (%) 4 12.6 0 2 1 0% 0.4 6.22 3.44 -40 1.66 0 6 12 18 π (mN/m) 80 b C0/a = 8 1.66 40 Derr (%) 0.29 -40 0.4 0.25 0 2 0% 1 0.45 4 1.01 0 0.5 t * 1 1.5 Fig. 6. Nondimensional diffusivity error (Derr) as a function of (a) the surface pressure (p) and (b) dimensionless time (t⁄) for C0/a = 0.4, 1, 2, 4, and 8.

concentrations and 0.7 mN/m at high concentrations in this study). The relationship between Derr and dimensionless time, t′ = t/[C2eq/(C20D)], at different surfactant concentrations is shown in Fig. 6b, in which Derr levels off as t′ increases at high concentrations. To determine these general benchmarks, the surfactant diffusiv- ity, estimated by the short-time approximation technique for dif- ferent surfactant concentrations, was initially investigated as a function of the surface pressure, p = c0–c. Fig. 7a shows the limit- ing conditions (pmax) for which the deviation between capprox (from the short time approximation straight line) and cdata(t) (from the Ward–Tordai equation) is allowable (Dc(t) < 0.1 and 0.7 mN/m at low and high concentrations). Fig. 7a shows the region (below the curve of pmax vs. C0/a) where the short-time approximation is applicable (i.e., with a reasonable Dc(t)). The error in estimating the surfactant diffusivity may range from 30% to 70% (Fig. 6), depending on the surfactant concentration C0/a and the region of cdata(t) used (indicating by p or t′). In order for the readers to apply the data (the region where the short-time approximation is appli- cable) easily, Fig. 7a are also shows this dependence in dimension- less parameters p′max (=pmax c0 ceq) and t′max (=tmax/[C2eq/(C20D)])

2**as a function of surfactant concentration C0/a.**

Dimensionless time t′max indicates the time t′ where p′ reaches p′max. Interestingly, as illustrated in Fig. 7b, a linear dependence (pmax vs. C0/a) was observed at low surfactant concentrations (C0/a 6 6). The existence of a linear dependence is probably because the sur- factant concentration is low. It is noted that this linear dependence in term of dimensionless parameter (p′max vs. C0/a and t′max vs. C0/a) works only at 0.4 6 C0/a 6 6. At an extremely low concentration (C0/a 6 0.4), both p′max and t′max decrease as concentration increases. a 20 π*max πmax (mN/m) 10 πmax 0 t*max 0.01 0.1 C0 / a 1 10 πmax (mN/m) 10 20 0.8 0.6 π*max 0.4 0 C0/a 4 20 πmax 10 8 1.8 1 t*max 0.2 b 0 0 2 C0 / a 4 0 0 4 C0/a 8 6 2.6 1.8 t*max 1 0.2 1.8 t*max 1 0.2 0.8 0.4 π*max 0 0.8 π*max 0.6 0.4 Fig. 7. (a) Conditions (maximal surface pressure pmax, dimensionless time t′max, and dimensionless surface pressure p′max) under which the short-time linear approxima- tsiuornfatcetcahnntisqwueitihssauprpfalicctaabnlteaacstaivfiutinecstoiofna o=f1su(srfa,ceta),n5t (c+o,nhce)natnrdat2io0n(DC0,/raf)o(r1d0iff9emreonlt/ cm2); (b) conditions for surfactant concentration C0/a 6 6. A simple linear dependence can be used to determine the limiting working conditions of the short-time approximation: p max ¼ 2:80ðC0=aÞ þ 0:72 ½¼ŠmN=m ð13Þ tmax ¼ 0:21ðC0=aÞ þ 0:12 ½¼Š ð14Þ p max ¼ 0:066ðC0=aÞ þ 0:33 ½¼Š ð15Þ For surface pressures greater than this maximal surface pres- sure, p > pmax, the dynamic surface tension curve deviates signifi- cantly from the linear region of the short-time approximation, and thus, the linear fitting of the tension could lead to significant errors in the calculated diffusivity. Therefore, Eq. (13) defines the range

16**of applicability of the short-time**

linear approximation tech- nique

12**in terms of the** surface pressure **as a function of** surfactant **concentration**

C0/a. A further analysis was conducted

18**to evaluate the** possible **effect of** the **surfactant** activity **on the**

nondimensional error in the diffu- sivity evaluated from the short-time approximation technique. As illustrated in Fig. 8, the Derr–c curves for different a values (a = 1 10 9, 5 10 9 and 20 10 9 mol/cm3), but the same sur- factant concentration C0/a, present a distinct trend. It can therefore be concluded that the surfactant activity plays only a minor role in obtaining a valid diffusivity estimate. 4. Discussion Based on the definition of the Ward–Tordai equation in Eq. (6) and the assumption that Eq. (9) is valid when surfactant backward diffusion can be assumed to be negligible, it is trivial to show how the deviation of c from the linear fitting is related to the actual 0 0% Derr (%) -10 a C0/a=0.4 -20 -30 72 71 γ 70 Derr (%) 0 -10 b C0/a=2 0% 10 40 Derr (%) 20 c C0/a=6 60 7 2 70 γ 68 66 0 0% 7 2 66 γ 60 54 Fig. 8. A nearly unique nondimensional error in diffusivity Derr evaluated from the short-time approximation technique as function of surface tension [c (t) range used for the linear short-time approximation fitting] for different surfactant activities a = 1 (s), 5 (r), and 20 ( ) (10 9 mol/cm3) at surfactant concentrations of C0/a = 0.4 (a), 2 (b), and 6 (c). balance between the forward and backward surfactant mass trans- port processes. To enhance understanding of this crucial aspect, both TermF (=2C0(Dt/p)1/2, Fig. 9a, solid curves) and TermB (=2(D/p)1/2 R ptffi CSðt sÞdpffisffiffi; Fig. 9a, dashed curves) of the 0 Ward–Tordai equation were calculated, using the Langmuir iso- therm (C1 = 5

6**10 10 mol/cm2, a** = 1 **10** 9 **mol/cm3,**

and Dset = 5 10 6 cm2/s), for three different surfactant concentrations. As clearly shown in Fig. 9a, after a rather short initial time interval, the backward diffusivity can no longer be omitted. Indeed, it is worth noting that even for time ranges close to t = 0, TermB is not null and a small degree of backward diffusion occurs. The relative importance of the backward diffusivity compared to the forward diffusivity is also clearly illustrated in Fig. 9b, in which the TermB/TermF ratio is analyzed: for time intervals t > 100s the diffusion of the surfactant from the sublayer to the bulk phase must be considered, and the use of the short-time linear approximation technique should not be considered to be com- pletely accurate. Finally, we compared all of the diffusivity data, estimated using the short-time linear approximation technique and reported in the literature, with the limiting criteria identified in this study. Fig. 10 shows the surface pressure p as function of surfactant concentra- tion C0/a for the data presented in Table 1. The maximum error limiting criteria (solid curve) and the criteria indicating a 30% error in diffusivity (dashed curve) were analyzed. It is noteworthy that the majority of the reported diffusivity data appear to be included Termi (10-10 mol/cm2) 8 6 4 0 Termi (10-10) 6 0 0 2 a C0/a = 8F 8 B 3 0.4 t* 2F 2 B 6 C0/a = 8F 8 B 2 F 2B 0.4 10 12 1 10 102 t (s) 103 0.6 C0/a=0.4 C0/a = 8 2 TermB / TermF 0.6 TermB / TermF 8 0.3 0.4 0 0 3 t* 6 2 0.2 b 0.4 0 1 10 102 t (s) 103 Fig. 9. (a) Forward diffusion (solid curves) and backward diffusion (dashed curves) determined from the Ward-Tordai equation and (b) the ratio of backward diffusion (TermB) to forward diffusion (TermF)

18**as a function of time** (main figure) **and** dimensionless **time** (inset); **t/**

t′ = 25,500, 5560, and 617 for C0/a = 0.4, 2.0 and 8.0, respectively. in our error limiting criteria, with the following error range for the estimated diffusivity coefficient: 30% < Derr < 30%. Regarding the various data reported in the literature that were observed to fall above our maximum limiting criteria, special attention is

required. Specifically, we do not claim that the surfactant diffusivities esti- mated by the authors who furnished these data are actually affected by errors to a great extent, but the fact that these points are far above our limit certainly suggests that the fundamental assumptions that led to our criteria (planar gas–liquid surfaces, diffusion-controlled mass transport process and Langmuir adsorp- tion isotherm) may not be applied for these specific systems. In this work, a fixed diffusivity (Dset = 5 10 6 cm2/s) was set for all the theoretical simulation. This diffusivity was chosen because the most of small surfactants have a diffusivity closed to this value. It is noted that the choice of the Dset won't make any change on the conclusion and phenomenon presented in this manuscript because the data was presented in the variation per- centage (Derr), as shown in Figs. 6 and 8. This study considered only a planar air–water interface for sur- factants following the Langmuir adsorption isotherm (i.e., no inter- molecular

15**interaction between the adsorbed surfactant molecules** at surface). However, **the**

evaluation error using the short time approximation method depends not only on surfactant concentra- tion (C0/a), but also on the spherical curvature of air–water 20 15 π (mN/m) 10 5 0 73% 23 51% 27 28 29 38 30 35 31 1368 264 7768%% 80% 85% 35 27 31 88% 29 35 5% 27 38 37 30 28 32 16 38 -1% -44% -32% 22 2-217' 35 22 30% 27 30 30 28 19 27 27 1278 1177 15 19 27 29 19 29 0.1 1 C 0 /a 10 100 Fig. 10. Comparison between literature data (in Table 1) and limiting surface pressure p criteria proposed in this work as function of C0/a. The criteria are evaluated for maximum limiting criteria (solid curve) and for 30% < Derr < 30% (dashed curve). Literature data shown in circles were obtained by pendant drop or maximum bubble pressure measurement methods, data shown in squares were obtained by the Wilhelmy plate method, and data shown in diamonds were obtained by the short-time linear approximation technique but without passing through the initial point of c0 = 72 mN/m at t = 0. The numbers shown near (or inside) the symbols indicate the reference articles. The numbers shown near the line indicate the theoretical percentage of diffusivity error. interface and the intermolecular interaction force. The applicability criteria for these more complicated systems have been studied and in the course of the article writing in our laboratory for the time being. 5. Conclusions The short-time approximation technique is widely used for lin- early fitting experimental dynamic surface tension data to estimate the diffusivity and to determine the adsorption mechanism of a given process. However, because it is assumed that at the beginning of the adsorption process, surfactant backward diffusion from the sublayer to the bulk phase is negligible and ffitffiCS is constant, the p applicability of this technique is limited to specific time intervals. Therefore,

2**in this work, a theoretical** numerical **simulation of the short-time approximation** technique **was conducted,** and general criteria **for**

its accurate utilization were analyzed. Specifically, for systems assuming planar gas–liquid surfaces, a diffusion-controlled mass transport process and a Langmuir adsorption isotherm, some simple rules were established in terms of maximal

4**surface pressure** pmax **and** maximal **dimensionless time** tm⁄ax **as a function of** the **dimensionless surfactant concentration** C0 **/a.**

For p > pmax or t > t/max, the dynamic surface tension curve deviates from the linear region of the short-time approximation, and thus, the linear fitting of the surface tension could lead to significant errors in diffusivity estimates. Under these conditions, thus, the actual applicability of the short-time linear approximation method must be critically evaluated. Conflict of interest None declared. Acknowledgments The authors would like to express great appreciation to Taiwan NSC and the Italian National Research Council for the support within the project ‘‘Mixed Particle-Surfactant Layers at Liquid Interfaces’’ (NSC/CNR Bilater Agreement 2014-2015 and NSC-100-2221-E-011-101). References [1] B.E. Chistyakov, Theory and practical application aspects of surfactants, Surfactants Chem. Interfacial Prop. Appl. (2001) 511–618. [2] Acmite Market Intelligence, Market Report: Global Surfactant Market, 2013. [3] S.S. Dukhin, R. Miller, G. Kretzschmar, On the theory of adsorption kinetics of ionic surfactants at fluid interfaces, Colloid Polym. Sci. 269 (1991) 923–928. [4] A.F.H. Ward, L. Tordai, Time-dependence of boundary tensions of solutions I. the role of diffusion in time-effects, J. Chem. Phys. 14 (1946) 453–461. [5] R. Miller, A.V. Makievski, V.B. Fainerman, Dynamics of adsorption from solutions, Surfactants Chem. Interfacial Prop. Appl. (2001) 287–399. [6] R. Defay, J.R. Hommelen III, The importance of diffusion in the adsorption process of some alcohols and acids in dilute aqueous solutions, J. Colloid Sci. 14 (1959) 411–418. [7] R.S. Hansen, T.C. Wallace, The kinetics of adsorption of organic acids at the water-air interface, J. Phys. Chem. 63 (1959) 1085–1092. [8] R. van den Bogaert, P. Joos, Dynamic surface tensions of sodium myristate solutions, J. Phys. Chem. 83 (1979) 2244–2248. [9] C.D. Ampatzidis, E.-M.A. Varka, T.D. Karapantsios, Dynamic surface properties of eco-friendly phenylalanine glycerol ether surfactants at the W/A interface, Colloids Surf. A Physicochem. Eng. Asp. 441 (2014) 872–879. [10] M. Eftekhardadkhah, P. Reynders, G. Øye, Dynamic adsorption of water soluble crude oil components at air bubbles, Chem. Eng. Sci. 101 (2013) 359–365. [11] S. Ferdous, M.A. Ioannidis, D. Henneke, Adsorption kinetics of alkanethiol- capped gold nanoparticles at the hexane–water interface, J. Nanoparticle Res. 13 (2011) 6579–6589. [12] T.D. Gurkov, Adsorption kinetics under the influence of barriers at the subsurface layer, Colloid Polym. Sci. 289 (2011) 1905–1915. [13] K. Sakai, S. Umezawa, M. Tamura, Y. Takamatsu, K. Tsuchiya, K. Torigoe, et al., Adsorption and micellization behavior of novel gluconamide-type gemini surfactants, J. Colloid Interface Sci. 318 (2008) 440–448. [14] A.M. Díez-Pascual, A. Compostizo, A. Crespo-Colín, R.G. Rubio, R. Miller, Adsorption of water-soluble polymers with surfactant character. Adsorption kinetics and equilibrium properties, J. Colloid Interface Sci. 307 (2007) 398–404. [15] T. Yoshimura, A. Sakato, K. Tsuchiya, T. Ohkubo, H. Sakai, M. Abe, Adsorption and aggregation properties of amino acid-based N-alkyl cysteine monomeric and N, N’-dialkyl cystine gemini surfactants, J. Colloid Interface Sci. 308 (2007) 466–473. [16] Y.A. Gao, W.G. Hou, Z.N. Wang, G.Z. Li, B.X. Han, G.Y. Zhang, Dynamic surface tensions of fluorous surfactant solutions, Chinese J. Chem. 23 (2005) 362–366. [17] C. Delgado, M.D. Merchán, M.M. Velázquez, S. Pegiadou, L. Pérez, M. Rosa Infante, The adsorption kinetics of 1-N-l-tryptophan-glycerol-ether surfactants at the air-liquid interface. effect of surfactant concentration and alkyl chain length, Colloids Surfaces A Physicochem. Eng. Asp. 233 (2004) 137– 144. [18] J.M. Rodriguez Patino, C. Carrera Sanchez, S.E. Molina Ortiz, R. Rodriguez Nino, C. Anon, Adsorption of soy globulin films at the air–water interface, Ind. Eng. Chem. Res. 43 (2004) 1681–1689. [19] U.R.M. Kjellin, J. Reimer, P. Hansson, An investigation of dynamic surface tension, critical micelle concentration, and aggregation number of three nonionic surfactants using NMR, time-resolved fluorescence quenching, and maximum bubble pressure tensiometry, J. Colloid Interface Sci. 262 (2003) 506–515. [20] E. Alami, K. Holmberg, J. Eastoe, Adsorption properties of novel gemini surfactants with nonidentical head groups, J. Colloid Interface Sci. 247 (2002) 447–455. [21] R. Rodriguez Nino, J.M. Rodriguez Patino, Effect of the aqueous phase composition on the adsorption of bovine serum albumin to the air–water interface, Ind. Eng. Chem. Res. 41 (2002) 1489–1495. [22] M.G. Munoz, F. Monroy, F. Ortega, R.G. Rubio, D. Langevin, Monolayers of symmetric triblock copolymers at the air–water interface. 2. adsorption kinetics, Langmuir 16 (2000) 1094–1101. [23] B.V. Zhmud, F. Tiberg, J. Kizling, Dynamic surface tension in concentrated solutions

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Casandra

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1et al. / International Journal of Heat and Mass Transfer 90 (2015)

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1et al. / International Journal of Heat and Mass Transfer 90 (2015)

752–760 759 760 A. Casandra et al. / International Journal of Heat and Mass Transfer 90 (2015) 752–760